

Polyfluoroallyl Cations ¹

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Polyfluoropropenes ($\text{CF}_3\cdot\text{CF}=\text{CFX}$) have been treated with antimony pentafluoride in sulphur dioxide at low temperatures. When $\text{X} = p\text{-MeO}\cdot\text{C}_6\text{H}_4$, both *cis*- and *trans*-isomers gave the same long-lived allyl cation, which was observed by n.m.r. spectroscopy; quenching with methanol gave methyl 2,3-difluoro-3-(*p*-methoxyphenyl)acrylate. In the case $\text{X} = \text{OMe}$, there is some C-1, C-3 interaction in the observed allyl cation; in the cases $\text{X} = \text{Ph}$ or Me species were obtained which were not characterised. A long-lived ion was not observed with hexafluoropropene but dimerisation occurred. Cyclobutenium ions have been generated from 1,2-dimethyl- and 1,2-dimethoxy-3,3,4,4-tetrafluorocyclobutenes; these ions have charge concentrated at C-1 and C-3.

THERE are now recorded a number of direct observations of systems with fluorine atoms directly attached to a carbocation.² It is well established that the destabilis-

ing electron withdrawal, $^+\text{C}\rightarrow\text{F}$, can be offset by meso-

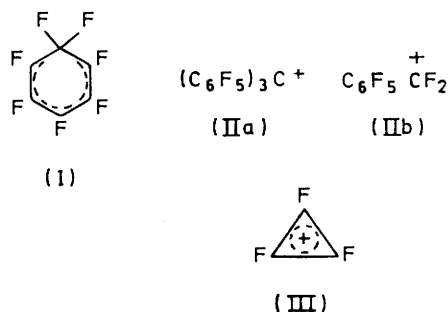
meric electron release, $\overset{\curvearrowright}{\text{F}}-\text{C}^+$, but that fluorine is strongly destabilising when not directly attached to the carbocation centre, *e.g.* $\text{F}-\text{C}-\text{C}^+$.³ Therefore, in principle,

¹ Preliminary communication, R. D. Chambers, R. S. Matthews, and A. Parkin, *J.C.S. Chem. Comm.*, 1973, 509.

² G. A. Olah and Y. K. Mo, *Adv. Fluorine Chem.*, 1973, 7, 69, and references therein.

³ R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley-Interscience, New York, 1973, ch. 4.

observation of long lived carbocations containing a number of fluorine atoms is feasible providing that, where possible, the fluorine atoms are attached to carbon atoms directly conjugated with the carbocation. Indeed, evidence has been presented for the observation

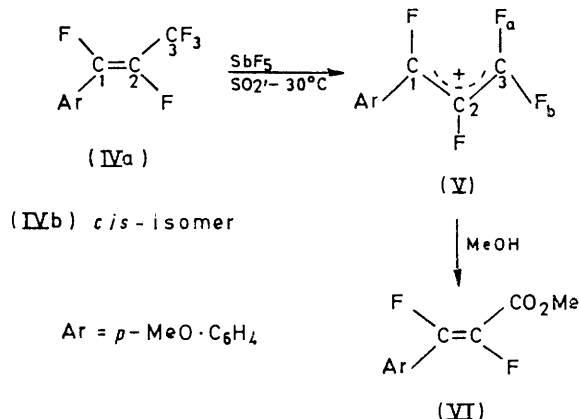


of a perfluorobenzenium ion (I)⁴ and related species² (although these systems may be complicated by the concomitant formation of radical cations); the perfluoroaryl systems (IIa)⁵ and (IIb);⁶ and the cyclopropenium system (III).⁷ In this paper we report the generation and direct observation of some polyfluorinated allyl systems.

Using techniques developed by Olah and his co-workers,² we have treated various fluorinated compounds with antimony pentafluoride, at low temperature, with sulphur dioxide as solvent. Reaction with *trans*-pentafluoro-1-(*p*-methoxyphenyl)propene (IVa) in sulphur dioxide at -30°C generated a long-lived species which could be studied by n.m.r. Four distinct fluorine resonances were observed (see Table I), each of intensity 1, indicating that ionisation had occurred, and this was confirmed by the large downfield shift of the F-1 signal, in comparison with the covalent starting material. Assignments were made on the basis of observed coupling constants, the largest value being attributed to a geminal F,F-coupling, $J_{3a,3b}$, and the F-2 signal was identified by the large couplings with both F-3a and -3b. Furthermore the large value of $J_{1a,3a}$ indicates that these fluorine atoms are in a *cis*-arrangement and is consistent with values of *peri*-F,F-couplings which have been observed in bicyclic aromatic systems.⁸ In the proton spectrum, significant downfield shifts were observed for the methoxy-group and ring protons. The *trans*-relationship of F-2 and F-1 in the ion (V) was confirmed by quenching the ion with methanol at -78°C , which gave the *trans*-ester (VI) in 62% yield. The fact that nucleophilic attack by methanol occurred exclusively at C-3 in the ion (V) is consistent with a range of fluoro-

olefin chemistry in which nucleophilic attack invariably occurs exclusively at a terminal difluoromethylene group.⁹ Further proof of ionisation from (IVa) came from the production of the same ion (V) from the *cis*-olefin (IVb), and subsequent quenching with methanol also gave the ester (VI).

The striking difference of over 100 p.p.m. between the chemical shifts for the fluorine atoms at positions 1 and 3 and the shift for F-2 in the ion (V), in itself, implies that there is less positive charge at C-2. Comparisons of chemical shifts for fluorine atoms in the ion (V) with values for the covalent starting material are only meaningful for C-1 and C-2, where no rehybridisation has taken place on ionisation. The F-1 signal occurs 94 p.p.m. further downfield from its position in the spectrum of the olefin (IVa), whereas the signal for F-2 is 6 p.p.m. further upfield. These observations demonstrate that charge is concentrated mainly at positions 1 and 3. However, although this is an established concept for allyl systems, there is relatively little direct experimental proof; indeed it has been suggested^{10,11} that there is significant interaction between C-1 and C-3 in the parent



allyl ion, to account for the apparent concentration of charge at the 2-position. However, in various cycloallylic ions,^{12,13} other than cyclobutenyl,¹³ C n.m.r. data demonstrate that charge is concentrated at C-1 and C-3.

The extent of the deshielding at F-1 in the ion (V) may be compared with a deshielding of 87.9 p.p.m. for the fluorine resonance in the ion $\text{CH}_3\cdot\overset{+}{\text{C}}\text{F}_2$, with respect to the precursor $\text{CH}_3\cdot\text{CF}_3$.¹⁴ Also, in the formation of ions from benzyldiyne fluoride and derivatives, the $\overset{+}{\text{C}}\text{F}_2$ fluorine nuclei are generally deshielded by *ca.* 70 p.p.m. with respect to the covalent precursors.¹⁵

⁹ R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, 1965, **4**, 50.

¹⁰ H. Simonetta and E. Heilbronner, *Theor. Chim. Acta*, 1964, **2**, 228.

¹¹ G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1964, **86**, 5682.

¹² G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, 1969, **91**, 3667.

¹³ G. A. Olah, J. S. Staral, and G. Liang, *J. Amer. Chem. Soc.*, 1974, **96**, 6233.

¹⁴ G. A. Olah and Y. K. Mo, *J. Org. Chem.*, 1972, **37**, 1028.

¹⁵ G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1969, **91**, 2955.

⁴ V. D. Shteingarts, Yu. V. Pozdnyakovich, and G. G. Yakobsen, *Chem. Comm.*, 1969, 1264; V. D. Shteingarts and Yu. V. Pozdnyakovich, *J. Org. Chem. (U.S.S.R.)*, 1971, **7**, 734.

⁵ G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1967, **89**, 1027.

⁶ Yu. V. Pozdnyakovich and V. D. Shteingarts, *J. Fluorine Chem.*, 1974, **4**, 283; 279.

⁷ P. B. Sargeant and C. G. Krespan, *J. Amer. Chem. Soc.*, 1969, **91**, 415.

⁸ R. D. Chambers, M. Hole, W. K. R. Musgrave, R. A. Storey, and B. Iddon, *J. Chem. Soc. (C)*, 1966, 2331.

Surprisingly, the reaction of pentafluoro-2-(*p*-methoxyphenyl)propene with antimony pentafluoride at -30°C gave a product with a very complex ^{19}F n.m.r. spectrum, which indicated the formation of a mixture of ionic species. Furthermore, quenching with methanol gave a mixture of products which we were unable to analyse. Both 1- and 2-phenylpentafluoropropenes gave, with antimony pentafluoride, systems that exhibited complex ^{19}F n.m.r. spectra, although integration did indicate that a fluoro-substituent had been removed.

TABLE 1
N.m.r. data for (IVa) and (V)

	$^1\text{H}^a$		$^{19}\text{F}^a$			
	OCH ₃	C ₆ H ₄	F(1)	F(2)	CF ₃ (3)	
(IVa)	δ 3.2	6.7	-147.9	-174.3	-68.2	
	$\{J_{1,2} 130; J_{1,3} 22; J_{2,3} 10.5 \text{ Hz.}\}$					
(V)	δ 3.7	7.3	-53.1	-180.6	-64.8	-68.6
	$[+0.5]^b$	$[+0.6]^b$	$[+94.8]^b$	$[-6.3]^b$	$[+3.3]^b$	$[-0.42]^b$
	$\{J_{1,2} 22; J_{2,3a} 97.5; J_{2,3b} 70.5; J_{1,3a} 59; J_{1,3b} 3; J_{3a,3b} 105.5 \text{ Hz.}\}$					

^a Values in p.p.m. from external CFCl₃ (^{19}F) or Me₄Si(^1H). ^b Shift with respect to (IVa).

A more unusual situation occurred with pentafluoro-1-methoxypropene (VII); ionisation clearly occurred with antimony pentafluoride and *cis*- and *trans*-isomers of (VII) gave the same species, but the n.m.r. spectra (Table 2) differed from those for the ion (V) (Table 1).

TABLE 2

	N.m.r. data for (VII) and (VIII)	
	$^1\text{H}^a$	$^{19}\text{F}^a$
(VII)	CH ₃ O 3.8	CF ₃ (3) -66.6
(VIII)	CH ₃ O 5.9 $[+2.1]^c$	CF ₂ -74.2(2) ^b $[-7.6]^c$
		F(2) -194.3
		F(1) -110.3
		[F(2), F(1)] $[-73.7(1),^b -76.4(1)^b]$
		$[+120.6, +33.9]^c$
		or $[+36.6, +117.9]^c$

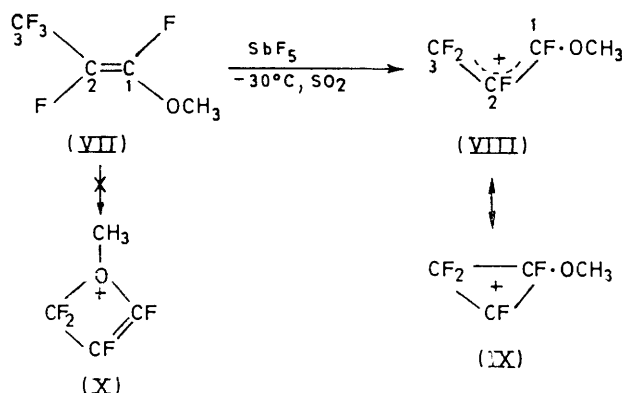
^a δ Values in p.p.m. from external CFCl₃ (^{19}F) or Me₄Si(^1H).
^b Integral ratio. ^c Shift with respect to (VII).

The differences are: (i) the individual ^{19}F resonances arising from the CF₂ group in (VIII) are not distinguishable, and (ii) although we were unable to distinguish between F-1 and F-2 in (VIII), nevertheless both of these nuclei are significantly deshielded with respect to the corresponding nuclei in (VII), in contrast to the observed upfield shift of the F-2 signal in the ion (V). Both these observations imply that there is more 1,3-interaction in the ion (VIII) than in (V), as represented by structure (IX). In principle, formation of (X) is also possible but we would anticipate a significant shift to low field for the CF₂ resonance arising from such a structure, in

comparison with CF₃ in the starting material (VII). Instead, there is a slight upfield shift. This is more understandable for an allyl system (VIII) where some rehybridisation at C-3 has occurred.

Hexafluoropropene (XI) reacted with antimony pentafluoride in sulphur dioxide, but the perfluoroallyl cation (XII) was not observed. Instead a dimer (XIII) was produced. This compound is readily obtained by the reaction of (XI) with fluoride ion,^{16,17} but its production in the presence of antimony pentafluoride seems more

likely to involve an electrophilic dimerisation, by a process similar to that observed with 3,3,3-trifluoropropene.¹⁸ Similar conclusions have been drawn by Russian workers,¹⁹ and it has also been established that perfluoroisopropylbenzene is produced from pentafluorobenzene and hexafluoropropene, in the presence of



antimony pentafluoride.²⁰ This is strong evidence that the perfluoroallyl cation (XII) is produced in this system, even though it is not sufficiently long-lived for direct observation.

We have also investigated the reactions of various polyfluorocyclobutenes with antimony pentafluoride in the hope of generating the fluorinated aromatic dication (XIV), or derivatives of it, since evidence has been presented^{21,22} for the direct observation of tetra-methyl and -phenyl analogues of (XIV). Nevertheless, the ^{19}F n.m.r. spectrum of perfluorocyclobutene was unaffected

¹⁶ R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc. (C)*, 1968, 2221.

¹⁷ W. Brunskill, W. T. Flowers, R. Gregory, and R. N. Haszeldine, *Chem. Comm.*, 1970, 1444.

¹⁸ P. C. Myhre and G. D. Andrews, *J. Amer. Chem. Soc.*, 1970, 92, 7595.

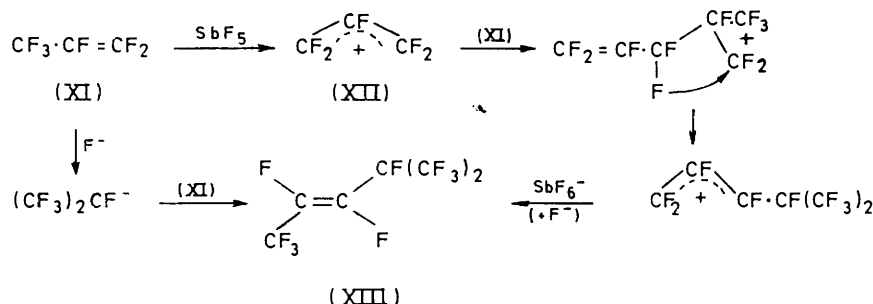
¹⁹ Yu. L. Kopaevich, G. G. Belen'kii, E. I. Mysov, L. S. German, and I. C. Knunyants, *Zhur. Vsesoyuz. Khim. obsch. im. D. I. Mendeleeva*, 1972, 17, 236 (*Chem. Abs.*, 1972, 77, 33864c).

²⁰ V. V. Brovko, V. A. Sokolenko, and G. G. Yakobson, *Bull. Acad. Sci. U.S.S.R.*, 1972, 21, 1630.

²¹ G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, 1969, 91, 3667.

²² G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, 1970, 92, 1430.

by the presence of antimony pentafluoride, even up to 100 °C. Replacing fluorine by other substituents, however, significantly enhanced reactivity, and the dimethyl derivative (XV) reacted at -30 °C, in sulphur dioxide. Ionisation was indicated by the presence of separate



signals from non-equivalent methyl groups in the ^1H spectrum and by CF and CF_2 signals in the ^{19}F n.m.r. spectrum with splitting patterns corresponding to the ion (XVI). Confirmation that ionisation had taken place came from the large (+133.8 p.p.m.) shift to low field of the F(c) signal as well as the marked change in coupling constants. Quenching of the ion (XVI) with

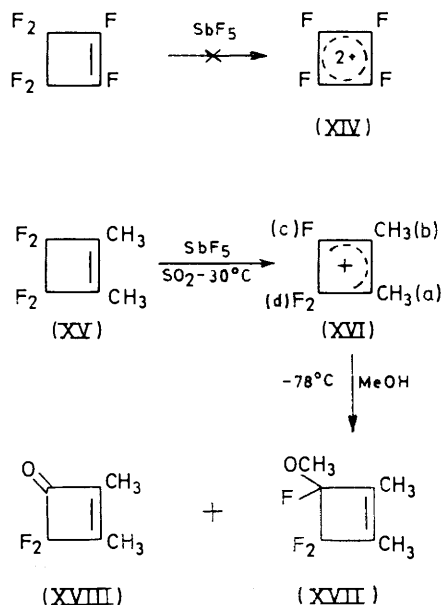


TABLE 3

N.m.r. data for (XV) and (XVI)	
(XV)	(XVI)
$^1\text{H}^a$	$^{19}\text{F}^a$
δ	δ
J_{HF}	
CH_3	CF_2
1.17	-115.6
1.25 Hz	
$\text{CH}_3(\text{a})$	$\text{CF}(\text{c})$
2.67	+18.2
[+1.50] ^b	[+133.8] ^b
$\text{CH}_3(\text{b})$	$\text{CF}_2(\text{d})$
1.67	-98.0
[+0.50] ^b	[+17.6] ^b

$J_{\text{ac}} 4.5$; $J_{\text{b,d}} 3.9$; $J_{\text{cd}} 10$ Hz.

^a δ Values in p.p.m. from CFCl_3 (^{19}F) or Me_4Si (^1H). ^b Shift with respect to (XV).

methanol at -78 °C gave mainly (XVII) and a trace of the derived ketone (XVIII).

A puzzling situation occurred in the reaction of the dimethoxy-analogue (XIX) with antimony pentafluoride. Two sets of signals (sets A and B), were produced which are each consistent with the ion (XX), except that set B occurs at lower field than set A. Nevertheless,

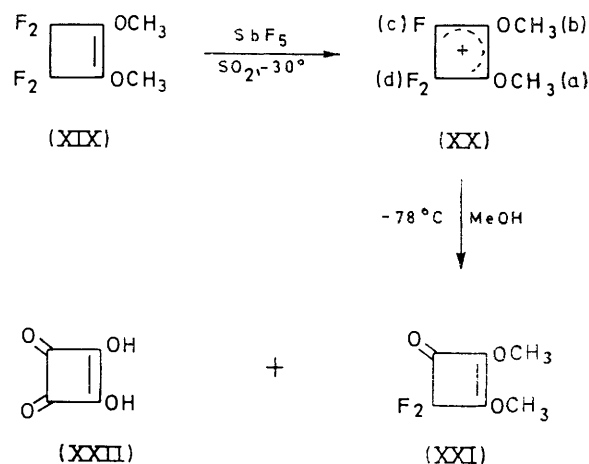


TABLE 4

(XIX)	$^1\text{H}^a$		$^{19}\text{F}^a$	
	OCH ₃ (a)	OCH ₃ (b)	CF(c)	CF ₂ (d)
	3.84		-111.4	
Set A	4.84	4.06	-41.1	-102.3
	[+1.00] ^b	[+0.22] ^b	[+70.3] ^b	[+9.1] ^b
Set B	4.64	4.06	-31.6	-86.5
	[+0.80] ^b	[+0.22] ^b	[+79.8] ^b	[+24.9] ^b

$J_{\text{FF}} 10.5$ Hz for both sets.

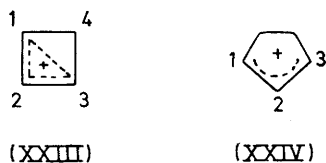
^a δ Values in p.p.m. for CFCl_3 (^{19}F) or Me_4Si (^1H). ^b Shifts with respect to (XIX).

together with the observation of F,F-coupling in both sets A and B, demonstrates that the ion (XX) is present. It is now clear, however, from the work of Smart and Reddy²³ that the two sets of signals arise from rotational isomers due to the methoxy-group at the (b) position in (XX). These workers,²³ using a 1 : 1 ratio of (XIX) : SbF_5 as opposed to our excess of SbF_5 , have successfully observed reversible variable temperature spectra, which

²³ Results kindly communicated by Dr. B. E. Smart. B. E. Smart and G. S. Reddy, *J. Org. Chem.*, forthcoming publication.

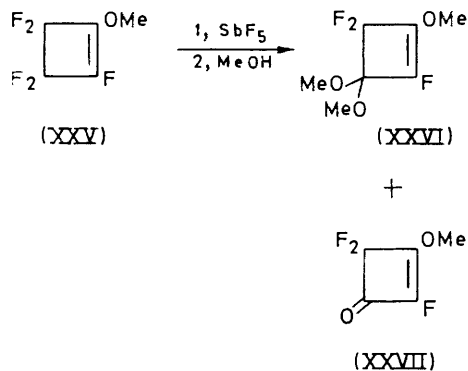
we were unable to achieve in our system. Quenching of (XX) with methanol at -78°C gives mainly the ketone (XXI), with a small amount of squaric acid (XXI). Since the ratio of signals A and B was *ca.* 2 : 1 it appears that quenching of the species responsible has given the same product.

Olah and his co-workers have presented evidence that the cyclobutenium ion exists as the homocyclopropenium structure (XXIII),^{13,24} *i.e.* significant interaction occurs between C-1 and C-3. Part of the evidence stems from



the fact that greater deshielding occurs for C-2 than for C-1 or C-3 in (XXIII) but, in contrast, the cyclopentenium ion (XXIV) and corresponding derivatives of larger ring systems show little 1,3-interaction. However, there is no basis for suggesting 1,3-interactions in the fluorinated cyclobutenium systems (XVI) or (XX), since chemical shifts show that charge is concentrated at C-1 and C-3.

Addition of the monomethoxy-derivative (XXV) to a solution of antimony pentafluoride in sulphur dioxide gave a solution whose n.m.r. spectrum we are unable to interpret. Quenching with methanol, however, gave the products (XXVI) and (XXVII), and this implies that ionisation had occurred.



EXPERIMENTAL

^1H and ^{19}F N.m.r. spectra were recorded with a Varian A56/60D instrument, operating at 60 and 56.4 MHz, respectively; ^{19}F shifts are in p.p.m. to low field from CFCl_3 .

General Method for Preparation of Ions.—An n.m.r. tube was cooled to -78°C and sulphur dioxide was condensed in to a depth of *ca.* 3 cm; small amounts of antimony pentafluoride (0.3–0.4 g) were then added and the tube was carefully shaken. The olefin was then added dropwise in a quantity such that the molar ratio of antimony pentafluoride to olefin was *ca.* 5 : 1. The tube was then shaken carefully to produce a homogeneous solution or, if necessary

²⁴ G. A. Olah, J. S. Staral, R. J. Spear, and G. Liang, *J. Amer. Chem. Soc.*, 1975, **97**, 5489.

²⁵ J. D. Park, M. L. Sharrar, and J. R. Lacher, *J. Amer. Chem. Soc.*, 1949, **71**, 2337.

to avoid over-heating, thorough mixing was brought about by agitation with a length of fine capillary tubing.

Preparation of Materials.—(1) *Pentafluoro-1-(p-methoxyphenyl)propene* (IV). With ethylene bromide as initiator, a Grignard reagent was prepared by addition of *p*-bromoanisole (20.5 g, 110 mmol) to magnesium turnings (3.0 g, 123 mmol) in dry ether (80 ml). The mixture was heated under reflux for 30 min, then the flask was cooled in liquid air and evacuated. Hexafluoropropene (15 g, 100 mmol) was transferred into the flask, under vacuum, and the apparatus was allowed to warm to room temperature while attached to a rubber bladder. The mixture was set aside overnight, after which reaction appeared to be complete, then hydrolysed with dilute hydrochloric acid. The resulting solution was extracted with ether; the ether layer was washed with aqueous sodium hydrogen carbonate, dried (MgSO_4), and evaporated under vacuum leaving a liquid (12.5 g) which was partially purified by vacuum transfer. Isomers were separated by preparative-scale g.l.c. (silicone oil; 160°C), giving *cis-pentafluoro-1-(p-methoxyphenyl)propene* (IVb), b.p. $> 200^{\circ}\text{C}$ (Found: C, 50.5; F, 39.9%; *M*, 238. $\text{C}_{10}\text{H}_7\text{F}_5\text{O}$ requires C, 50.4; F, 39.9%; *M*, 238); and the *trans-isomer* (IVa) (Found: C, 50.5; F, 39.5%; *M*, 238).

(2) *Pentafluoro-1-methoxy- and Tetrafluoro-1,2-dimethoxycyclobutenes*. The method described²⁵ for the preparation of these cyclobutenes was modified in that the perfluorocyclobutene was introduced, with an inflatable rubber bladder, rather than by the more wasteful bubbling of olefin through the reaction mixture.

(3) *Tetrafluoro-1,2-dimethylcyclobutene*. This was obtained by a reported method.²⁶

Quenching Reactions.—*General procedure.* Sulphur dioxide was condensed into a two-necked flask cooled to -78°C under dry nitrogen. Antimony pentafluoride was then introduced and the mixture was stirred. The olefin was added dropwise, with stirring, until a molar ratio of antimony pentafluoride to olefin of *ca.* 5 : 1 had been reached. The flask was then warmed to the temperature at which the n.m.r. spectrum of the ion had been previously recorded, and a sample of the mixture was taken into an n.m.r. tube in order to check that the ion had been generated. The flask was then re-cooled to -78°C and dry methanol (pre-cooled to -78°C) was added, dropwise. This addition was carried out cautiously because a vigorous reaction usually occurred. After an excess of methanol had been added, solutions which had exhibited intense colour had become colourless. The solution was then allowed to warm to room temperature and poured into dry ether. This solution was poured into water, and further washing of the ether layer with aqueous sodium hydrogen carbonate was carried out. Particular caution was required at this stage, since the ether contained significant quantities of dissolved sulphur dioxide and vigorous effervescence occurred. The ether layer was dried (MgSO_4), and ether was removed by fractional distillation.

(1) *trans-Pentafluoro-1-(p-methoxyphenyl)propene* (IVa). Quenching a solution containing (IVa) (5 g, 21 mmol) gave *methyl 2,3-difluoro-3-(p-methoxyphenyl)acrylate* (VI) (3.0 g, 63%), m.p. $72-72.5^{\circ}$ (from hexane) (Found: C, 57.6; H, 4.5; F, 16.4%; *M*, 228. $\text{C}_{11}\text{H}_{10}\text{F}_2\text{O}_3$ requires C, 57.9; H, 4.4; F, 16.65%; *M*, 228), ν_{max} 1750 (C=O) and 1690 cm^{-1} (C=C); ^{19}F δ -164.2 and -135.4 . The *trans*-structure was shown by the large value for J_{FF} (130 Hz).

²⁶ S. Dixon, *J. Org. Chem.*, 1956, **21**, 400.

Identical results were obtained with the *cis*-isomer (IVb).

(2) *Tetrafluoro-1,2-dimethylcyclobutene* (XV). Quenching a solution of the olefin (XV) (2.5 g) gave a mixture (1.5 g) containing two major components. These were separated by preparative-scale g.l.c. (150 °C; di-*n*-decyl phthalate). The minor component was 4,4-difluoro-2,3-dimethylcyclobuten-2-one (XVIII) (0.3 g), *M* 132, ν_{\max} 1780 cm^{-1} (C=O); ^{19}F δ -110.8, ^1H δ 1.99 and 2.30 (CH_3). The major product could not be obtained analytically pure but was identified as 3,3,4-trifluoro-4-methoxy-1,2-dimethylcyclobutene (XVII) (1.0 g) on the basis of n.m.r. data [^{19}F δ -111.26 and -115.3 (1:2), ^1H δ 1.56 and 1.71 (CH_3)]. The mass spectrum did not show a parent peak at *m/e* 166, but showed a peak at *m/e* 132, corresponding to loss of CH_3F , and a fragmentation pattern similar to that observed for (XVIII).

(3) *Pentafluoro-1-methoxycyclobutene*. Quenching a solution containing the olefin (5.0 g) gave a product (3.7 g) which consisted of two major components. These were separated by preparative-scale g.l.c. (di-*n*-decyl phthalate; 120 °C). The minor component (0.3 g) was 2,4,4-trifluoro-3-methoxycyclobutenone (XXVII) (Found: C, 39.2; F, 36.8%; *M*, 152. $\text{C}_5\text{H}_3\text{F}_3\text{O}_2$ requires C, 39.5; F, 37.5%; *M*, 152), ν_{\max} 1810 cm^{-1} (C=O); ^{19}F δ -141.7 and -118.2 (1:2), ^1H δ 4.24 (OCH_3). The major component (2.7 g)

was 1,3,3-trifluoro-2,4,4-trimethoxycyclobutene (XXVI), b.p. 169° (Found: C, 42.8; F, 28.4%; *M*, 198. $\text{C}_7\text{H}_9\text{F}_3\text{O}_3$ requires C, 42.4; F, 28.8%; *M*, 198), ^{19}F δ -135.2 and -117.0 (1:2), ^1H δ 3.42 (OCH_3) and 2.86 (2 OCH_3).

(4) *Tetrafluoro-1,2-dimethoxycyclobutene*. Quenching the mixture containing this olefin (XIX) gave a mixture which could not be separated. However, the ^{19}F n.m.r. spectrum showed only one fluorine singlet at -110.2 p.p.m. (CF_2); the mixture was hydrolytically unstable, giving squaric acid,²⁷ identified by comparison (i.r. spectrum) with an authentic sample.

Reaction of Hexafluoropropene with Antimony Pentafluoride.—A mixture of hexafluoropropene (2.5 g, 17 mmol) and antimony pentafluoride (18 g, 83 mmol) was heated in an evacuated Carius tube for 20 min at 70 °C. Volatile products (2.2 g) were then transferred from the tube under vacuum. The product contained dissolved hexafluoropropene and two other components; these were separated by preparative-scale g.l.c. (25 °C; di-*n*-decyl phthalate) and identified as 2*H*-heptafluoropropane,²⁸ *M* 169, and a dimer (XIII) of hexafluoropropene,²⁹ *M* 300, identified by comparison of spectra with those of authentic samples.

We thank the S.R.C. for a grant (to A. P.).

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